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Journal:	<i>Langmuir</i>
Manuscript ID	la-2018-02846s.R2
Manuscript Type:	Article
Date Submitted by the Author:	n/a
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Liquid cell transmission electron microscopy sheds light on the mechanism of palladium electrodeposition

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Abstract

Electrodeposition is widely used for fabricating tunable nanostructured materials in applications ranging from biosensing to energy conversion. A model based on 3D island growth is widely accepted in explaining the initial stages of nucleation and growth in electrodeposition. However, there are regions in the electrodeposition parameter space where this model becomes inapplicable. We use liquid cell transmission electron microscopy along with *post-situ* scanning electron microscopy to investigate electrodeposition in this parameter space, focusing on the effect of supporting electrolyte, and to shed light on the nucleation and growth of palladium. Using a collection of electron microscopy images and current time transients recorded during electrodeposition, we discover that electrochemical aggregative growth, rather than 3D island growth, best describes the electrodeposition process. We then use this model to explain the change in morphology of palladium electrodeposits from spherical to open clusters with non-spherical morphology when HCl is added to the electrolyte solution. The enhanced understanding of the early stages of palladium nucleation and growth and the role of electrolyte in this process provides a systematic route towards the electrochemical fabrication of nanostructured materials.

Introduction

Electrodeposition is a versatile method for fabricating coatings on conductive substrates. While traditionally this method has been used for creating aesthetic and/or anti-corrosion coatings in various manufacturing sectors; recently, there has been a rising interest in using electrodeposition for creating structures that are tunable over multiple length scales. The ability to create tunable nano and microscale structures and assemble them into three dimensional hierarchical architectures has proven to be critical in tuning the mechanical^{1,2}, electronic/electrochemical³⁻⁵, optical⁶⁻⁹, and surface properties⁷ of materials. Consequently, simulations and experimental studies are being intensely performed in order to design structures that have ideal morphologies and length scales for use in applications ranging from tissue engineering to energy conversion. Manufacturing such structures containing micro and/or nanoscale components is often achieved using top-down or bottom-up processes, or their combination. Among these, electrodeposition is ideally suited for the large volume and low-cost fabrication of structures with simple (nanowires¹², nanosheets¹³, hemispheres¹⁴) and complex (dendritic^{15,16}, fractal¹⁷, acicular¹⁸, globular assemblies¹⁹) architectures.

Due to its nobility, catalytic activity, and hydrogen reactivity, palladium is heavily investigated for use in emerging devices such as biosensors^{3,20}, biofuel cells²¹, and hydrogen fuel cells^{22,23}. Overpotential electrodeposition – deposition at potentials more negative than the equilibrium potential – of palladium is an effective strategy for developing 3D structures with tunable morphologies suitable for the abovementioned applications²⁴. Structural tunability is achieved by varying the applied potential/current waveform and the composition of the electrodeposition bath. Hydrochloric acid (HCl) is used as an electrolyte for tuning the structure of various materials (platinum²⁵, palladium²⁴, copper^{26,27}, zinc oxide²⁸, nickel²⁹, etc.) in electrodeposition. The role of

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3 HCl in structural tunability of metallic electrodeposits is attributed to the preferential adsorption
4 of chloride on specific crystalline planes during deposition^{30,31}, the influence of bath pH on the
5 equilibrium concentration of metallic ions in the solution³², and the impact of HCl concentration
6 on the overall deposition rate³³. In spite of existing studies on HCl-mediated *structural tunability*,
7 there is a need for additional studies on *structural evolution* of these electrodeposits to better
8 understand how HCl varies the structure of electrodeposits. In order to focus on structural
9 evolution, we used liquid cell transmission electron microscopy (TEM) to study the
10 electrodeposition of palladium *in-operando* and in its native environment.
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22 Liquid cell TEM has been used for studying the electrodeposition of copper^{34–39}, gold^{40,41}, and
23 lead⁴². Many of these studies are focused on correlating the *in situ* images and the measured current
24 time transients to the traditional electrodeposition models based on Volmer-Weber 3D island
25 growth⁴³. However, recent liquid cell⁴⁴ and identical location TEM⁴⁵ studies have shown that the
26 assumptions of negligible lateral diffusion and interaction between adjacent nuclei are not valid
27 during the initial stages of electrodeposition. Recently, a generalized electrochemical aggregative
28 growth mechanism has been proposed for the overpotential electrodeposition of platinum,
29 palladium, and silver on low surface energy substrates, which considers self-limited nanocluster
30 growth, nanocluster surface diffusion, and coalescence as the processes involved in structural
31 development of electrodeposits^{46–49}. Here we develop an integrated approach combining liquid cell
32 TEM, *post-situ* scanning electron microscopy (SEM), and electrochemical analysis to study the
33 overpotential deposition of palladium on low energy surfaces, where the traditional nucleation and
34 growth models are not applicable. This approach allows us to explain the mechanistic role of HCl
35 in structural tunability in the context of the aggregative electrodeposition growth model.
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Results and discussion

Palladium electrodeposition was performed using chronoamperometry, where a fixed DC potential was applied to the working electrode inside a liquid cell TEM setup. As shown in Figure 1, the system contained a miniaturized electrochemistry cell at the tip of a TEM holder, and was integrated with microfluidic and electrical circuitry. Using the microfluidic system, the electrolyte was flowed between two silicon nitride membranes, which permitted observation of the electrochemical reactions on the working electrode in *real-time*.

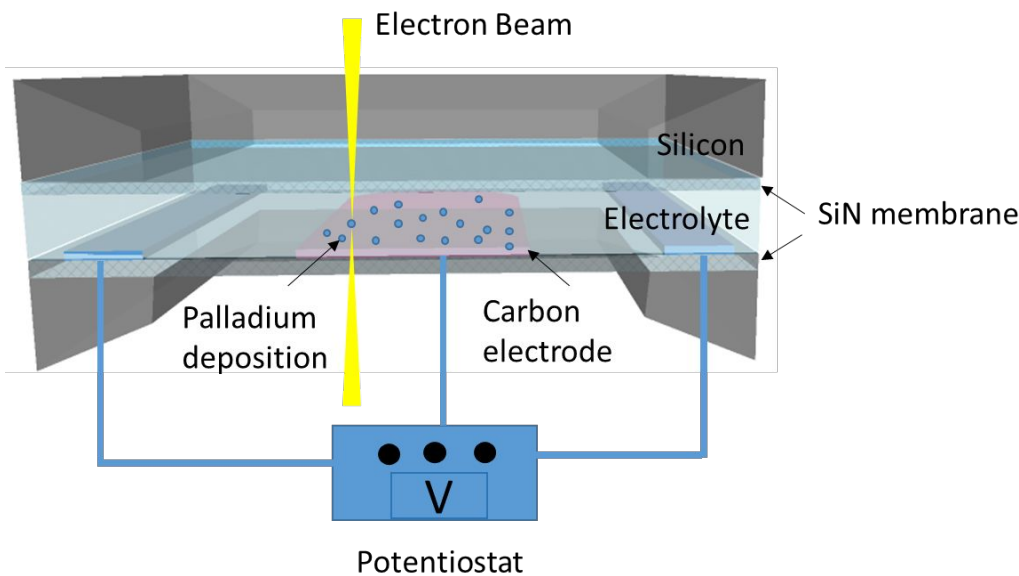


Figure 1. Schematic of the liquid cell TEM setup used for electrodeposition of palladium. The silicon chips have a silicon nitride membrane, and the bottom chip contains three electrodes (working, reference and counter) for performing electrochemistry. Palladium nanostructures are deposited on the carbon working electrode by applying a fixed potential.

To understand the effect of HCl on the structural evolution of palladium crystallites during electrodeposition, two different experiments were conducted. The first experiment was focused on the *in situ* electrodeposition of palladium on a carbon microelectrode from a solution of hydrogen chloropalladate (H_2PdCl_4), and the second one was performed by adding HCl to the H_2PdCl_4

precursor solution. We performed cyclic voltammetry in the two solutions and observed characteristic curves with peaks for palladium reduction, oxidation, and hydrogen adsorption/absorption and desorption (Supplementary Figure S1). Based on the measured open circuit potential and the CV profile, the overpotential used for in situ electrodeposition (-0.6 V versus Pt) was 0.605 V for 5 mM H_2PdCl_4 and 0.603 V for H_2PdCl_4 in 0.15 M HCl, which are both within the hydrogen adsorption/absorption region.

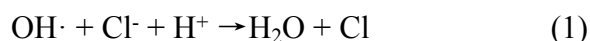
The time-resolved bright-field scanning transmission electron microscopy (BF-STEM) micrographs along with the current time transients (CTTs) obtained during these experiments are demonstrated in Figure 2 (the corresponding videos acquired during the *in situ* experiment are included as Supplementary Videos 1 and 2). In the case without HCl (Figure 2(a)), nucleation and growth were observed, initially (0 - 10 s), along the electrode edge. At deposition times of 30 s or larger, clusters started to appear on the inner electrode area. After 30 s of electrodeposition, palladium structures started to appear beyond the electrode edge. In the case with HCl, initially (0 - 10 s of deposition), the large majority of crystallites appeared along the edge of the electrode, and these edge-bound clusters finally grew into microscale clusters at 150 s. At longer times ($t \geq 10$ s), palladium deposits appeared in the inner area of the electrode; however, the amount of palladium (evaluated based on cluster size and surface density) electrodeposited in this area was significantly smaller than the amount present at the electrode edge at every time point. This behavior was also seen in the experiment without HCl; however, the enhanced deposition at the electrode edge is more pronounced in the case with HCl. Previous reports have indicated that the adsorption of chloride ions on the electrode surface retards the palladium electrodeposition process^{33,50}. However, this effect is dependent on the electrodeposition overpotential: at high overpotentials, the chloride concentration at the electrode surface tends to decrease, diminishing the chloride-

related retardation process³³. According to the electric field simulations performed on the miniaturized electrochemistry setup, we observe electric field enhancement at the electrode edges (Supplementary Figure S2). In both cases, with and without HCl, this field enhancement increases the deposition rate at the electrode edges. However, in the case with HCl, this field enhancement is expected to play an additional role, it overcomes the potential barrier caused by the adsorption of chloride ions at the electrode edge. This results in considerable difference in the amount of deposits present at the electrode edge and the inner electrode area.

Comparing the regions of the chip that were illuminated (Figure 2, 150 s) and were not illuminated (Figure 2, 150 s-no beam) by the electron beam during electrodeposition, we obtain interesting insights on the interplay between electrodeposition and electron beam-induced nucleation and growth. Under the influence of electron beam, the structures present at the electrode edge had a dendritic structure that is observed in diffusion-limited growth⁵¹. This is consistent with other reports suggesting that the electron beam can affect the electrochemical processes under investigation and increase the overall electrodeposition rate by generating reducing species through radiolysis^{35,52}, requiring the electron beam dose to be controlled to avoid local depletion of palladium ions^{53,54}. Another observation that is solely relevant to the case without HCl is that under the direct influence of electron beam, deposits were present on the silicon nitride window beyond the boundary of the carbon electrode. This suggests that adding HCl to the electrodeposition bath reduces the rate of beam-induced nucleation and growth.

We believe that the electron beam impacts the electrodeposition process differently in solutions with and without HCl due to the differences in solution pH and chloride ion concentration. The interaction of the electron beam with aqueous solutions results in the generation of highly reactive oxidizing ($\text{OH}\cdot$ and H_2O_2) and reducing (hydrated electrons, $\text{H}\cdot$, and H_2) species⁵⁵. Previous studies

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3 have shown that the ratio of hydrated electrons to hydroxide radicals decreases as the solution pH
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5 is decreased due to the rapid combination of hydrated electrons with hydrogen ions⁵². This suggests
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7 a decrease in beam-induced nucleation (*i.e.* beam-induced reduction of metallic ions) in solutions
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9 with a lower pH. Furthermore, in solutions with a high concentration of chloride ions, the primary
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11 radical $\text{OH}\cdot$ reacts with chloride ions resulting in the generation of $\text{Cl}_2\cdot^-$ (equations (1) and (2)),
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13 which is an oxidizing agent⁵⁶.
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24 Consequently, we expect the solution containing HCl to result in an environment that is more
25
26 oxidizing under the electron beam compared to the solution lacking HCl, making it more difficult
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28 for the beam induced reduction of metallic ions to occur.
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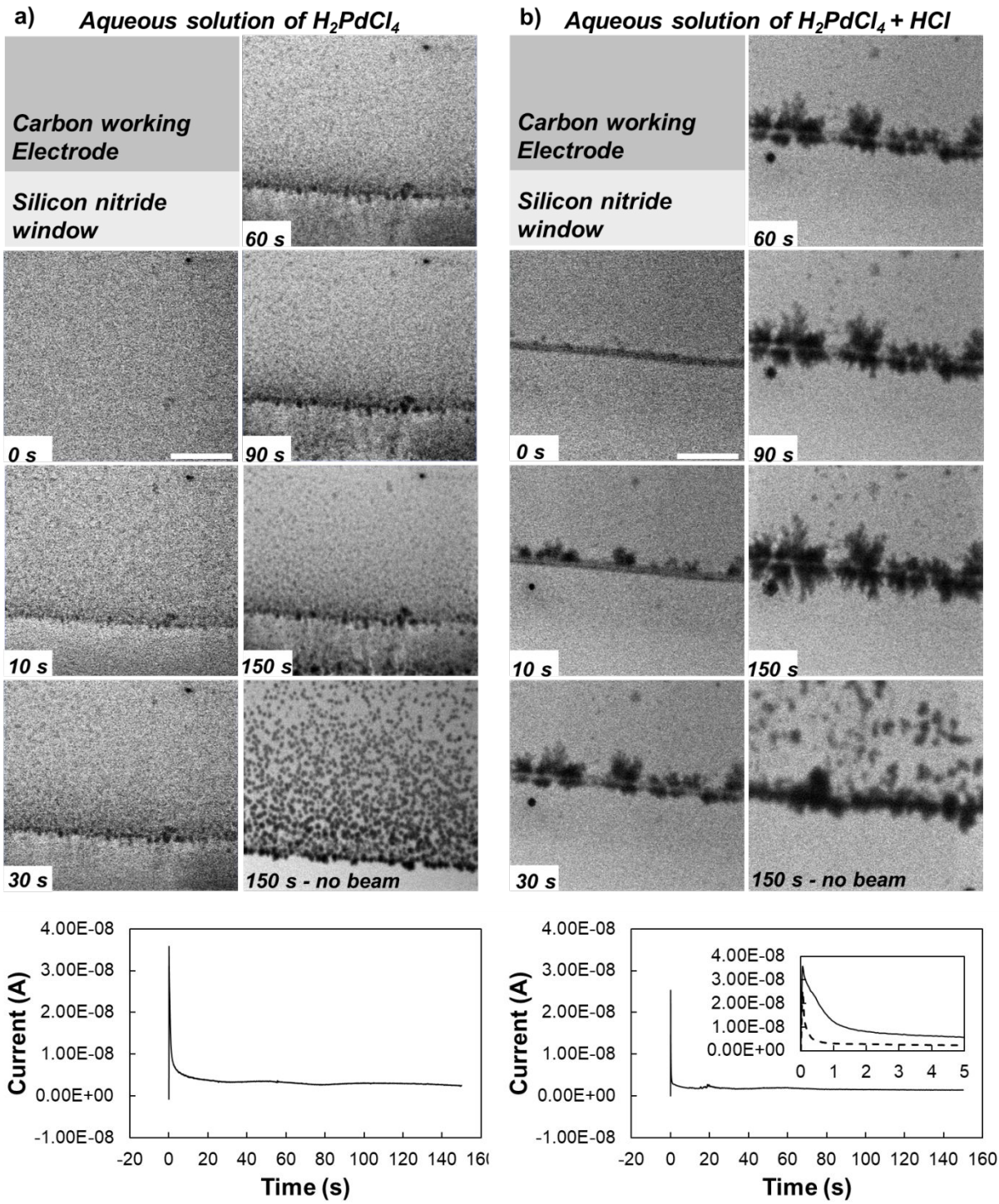


Figure 2. Electrodeposition of palladium inside liquid cell TEM with and without HCl. The top row schematic represents the orientation of microchips as seen in the images in this figure. BF-STEM

micrographs acquired at 0 s, 10 s, 30 s, 60 s, 90 s, and 150 s of deposition on a carbon electrode in a 5 mM H_2PdCl_4 bath without (a) and with 0.015 M HCl (b) under an applied potential of -0.6 V versus on-chip platinum reference electrode, flow rate of 5 $\mu\text{L}/\text{min}$, and a beam dose of 21 electrons/frame. nm^2 . The micrograph labeled as 150 s-no beam represents an image of an area of the chip not directly exposed to the electron beam following 150 s of electrodeposition. The image was acquired after turning off the electrical bias and replacing the electrodeposition bath with water. The bottom row represents the current time transients obtained during the liquid cell TEM experiments. The inset in the current time transients represents the 'with' (dotted) and 'without' (solid) HCl curves overlaid and zoomed in to show the first five seconds of deposition. Scale bar represents 1 μm .

To understand the cause of morphological differences induced by adding HCl, we compared the CTTs obtained during the *in situ* experiments of Figure 2. Since the chronoamperograms were obtained in the presence of the electron beam, we evaluated the effect of the beam on the shape of the acquired CTTs (Supplementary Figure S3). The curves obtained with and without the electron beam demonstrated very similar shapes indicating that the electron beam does not significantly alter the mechanism of electrodeposition. In addition, because the CTTs were obtained under fluidic flow, we performed a control experiment to compare the CTTs obtained with and without flow (Supplementary Figure S4). By introducing flow to the system, the measured current slightly increased, likely due to the enhanced mass transport; however introducing flow did not alter the shape of the acquired CTTs.

In both electrolytes, we observed a current decrease following the application of the potential step. In potential step experiments, this type of current decrease is often attributed to the double layer capacitive charging; however capacitive currents have time constants that are typically in the order of microseconds⁵⁷ rather than milliseconds or seconds. We sought to explain these results using the models developed by Scharifker and Hills (SH model). The SH model assumes that

hemispherical nuclei grow by direct attachment of ions, the ions are delivered to the nuclei by semi-infinite diffusion, and concentration of the electrodepositing ions is zero at the surface. The most significant feature of the SH model is that it predicts a current increase following the capacitive charging. This current increase is caused by the increase in the electroactive surface area as the number of nuclei increases and/or the nuclei grow in size⁴³. This behaviour was not observed in the CTTs demonstrated in Figure 2, which could be due to the experimental conditions used here. While the SH model assumes electrodeposition to occur under diffusion control, convection and migration could contribute to mass transport in our experimental setup due to the fluidic flow inside the liquid cell and the small concentration of supporting electrolytes used. In addition, under high overpotential, it is possible to obtain a high density of nuclei that cover the entire surface and result in a decaying current.⁵⁸ Given that the current decay was observed in the presence and absence of flow (Supplementary Figure S4), with and without supporting electrolyte (Supplementary Figure S5), and with HCl where low coverage was observed, we turned to an alternative model based on electrochemical aggregative growth, which is applicable to CTTs with monotonically decreasing currents⁴⁶. In electrochemical aggregative growth, electrodeposits are formed by self-limited growth of nanoclusters, overpotential-dependent nanocluster surface diffusion, and nanocluster coalescence/recrystallization^{46–49}. This differs from the conventional electrochemical nucleation and growth theories in that, while primary nuclei grow by direct adatom attachment, beyond a critical diameter, they grow by nanocluster aggregation and coalescence. To evaluate the suitability of this model for explaining the measured CTTs, we imaged the microchips used in the liquid cell TEM experiments using scanning electron microscopy (SEM) after the electrodeposition process. The *post situ* SEM images (Figure 3) confirm the observations obtained from liquid cell TEM (Figure 2). The amount of deposits

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3 increased at the electrode edge compared to the inner electrode area, and adding HCl to the
4 electrodeposition bath changed the structures from spherical to non-spherical deposits.
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6 Additionally, SEM micrographs demonstrate that the deposited areas, in the case with and without
7 HCl, contained small circular clusters (Supplementary Figure S6) even at long deposition times
8 (150 s). This dispersion in cluster size has been previously observed and suggested^{43,46} in the
9 aggregative growth model. The observed dispersion in nanocluster size, in addition to the
10 monotonically decreasing current in the CTT curves support the electrochemical aggregative
11 growth model. However, it should be noted that the electrochemical aggregative growth model has
12 not been previously studied when convection and migration contribute to mass transport in
13 addition to diffusion. It is possible that electrochemical Ostwald ripening⁵⁹ and progressive
14 nucleation and growth⁴³ also play a role in the growth of the clusters observed here; however,
15 liquid-cell TEM does not provide us with the required spatial or temporal resolution to differentiate
16 between these mechanisms.
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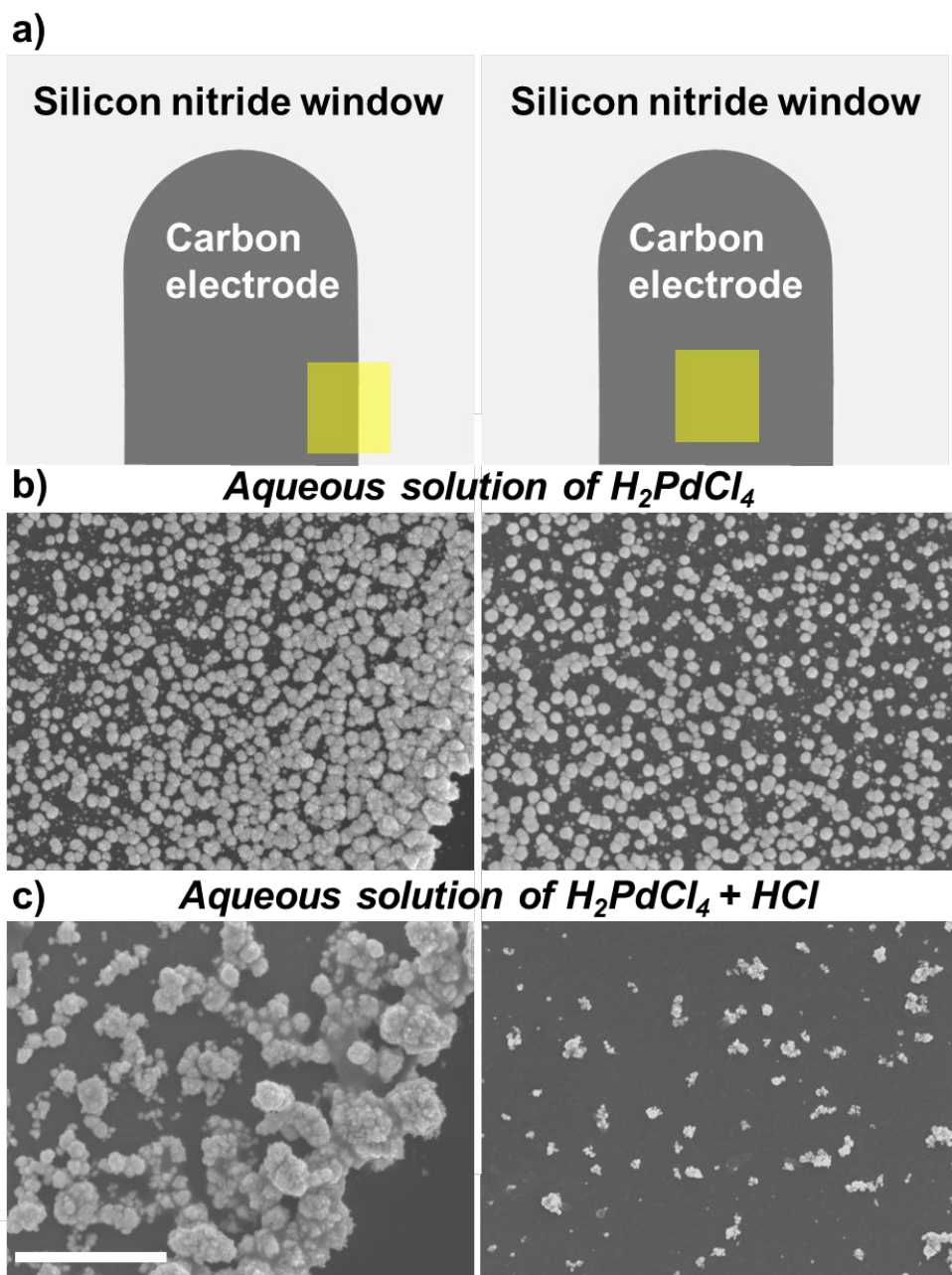


Figure 3. *Post situ* SEM imaging of the electrochemical chip used in liquid cell TEM experiment of Figure 2. The schematic drawing in (a) demonstrates the area imaged in (b) and (c). *Post situ* SEM micrographs of the chips used in Figure 2 without (b) and with (HCl). The images on the left demonstrate an area of the chip that contain the edge of the carbon electrode, while the images on the right show the middle part of the carbon electrode. Scale bar represents 1 μm .

Given the large electric fields experienced in miniaturized electrochemical cells (see simulations in Supplementary Figure S2), we looked into the potential effect of migration on the CTTs and images acquired during liquid-cell TEM experiments. For this purpose, we sought to eliminate migration effects by adding a large concentration of supporting electrolyte (500 mM KCl) to our H_2PdCl_4 baths (Supplementary Figure S5). Adding the supporting electrolyte significantly increased the magnitude of the current obtained during electrodeposition. In spite of this, the general shape of the CTTs and the morphology of the deposits did not change. Given our solution pH (≤ 2), PdCl_4^{2-} is the dominant Pd (II) species³². As a result, under our biasing conditions (working electrode negatively biased with respect to the counter electrode), migration effects would decrease the flux of these species to the negatively biased working electrode. It is possible that under electrochemical aggregative growth, migration effects do not significantly affect the morphology of the deposits because processes such as surface diffusion, aggregation, and recrystallization occur at or near the electrode, whereas migration mostly affects mass transport in the bulk.

After selecting a suitable theory for explaining the nucleation and growth of palladium clusters, we used this model to explain the role of HCl on the morphological development of the clusters. Previous studies suggest that recrystallization and coalescence kinetics, to a large extent, dictate the morphology of the final electrodeposits⁴⁶. Without HCl, we observed spherical clusters that were less porous and smoother than with HCl. Including HCl in solution, resulted in non-spherical clusters that had a porous and open morphology. This suggests that recrystallization and direct addition of palladium are less dominant in the case with HCl. We present two hypotheses for explaining the role of HCl in impeding the recrystallization and direct addition processes.

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3 1. It is known that at $\text{pH} < 5$, PdCl_4^{2-} is the dominant Pd (II) species, and the concentration of
4 this complex ion decays sharply in the 6-10 pH range, with a parallel increase in the
5 concentration of hydroxide-containing Pd (II) species³². In both solutions used for in situ
6 electrodeposition, with pH of 2.0 for 5 mM H_2PdCl_4 and 1.6 for 5 mM H_2PdCl_4 in 0.015
7 M HCl, PdCl_4^{2-} is the dominant species. The dissociation of PdCl_4^{2-} results in the
8 generation of adsorbed PdCl_2 species, which favours chloride ion adsorption at the
9 electrode³³. The adsorption of chloride is enhanced in the solution with HCl with increased
10 chloride ions. We expect this to result in the retardation of direct palladium addition in the
11 presence of HCl. The inhibiting role of HCl is also evident when we compare the integrated
12 charge calculated in solutions with and without HCl (Supplementary Figure S7). The
13 solution without HCl consistently resulted in a larger amount of integrated charge
14 indicating an overall increased disposition rate compared to the case with HCl.

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17 2. We performed electrodeposition at a potential (-200 mV versus Ag/AgCl) close to
18 the hydrogen adsorption/absorption potential (supplementary Figure S1). In this potential
19 range, there is competition between the adsorption and absorption of hydrogen species and
20 the direct attachment of palladium atoms⁶⁰. We expect this competition to be enhanced in
21 the electrolyte with a lower pH, and to decrease the direct addition of palladium atoms in
22 the HCl-containing solution.

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25 The first hypothesis was further validated by replacing HCl with KCl and keeping all other
26 conditions the same (Supplementary Figure S8). The non-spherical morphology was seen in the
27 clusters deposited using both chloride-containing electrolytes, confirming that chloride ions are
28 important for creating non-spherical clusters with a porous and open morphology. Comparing the
29 chronomaperomagrams obtained in solutions with HCl and KCl indicates that HCl yields a lower

deposition rate compared to KCl. This indicates that our second hypothesis, competition between hydrogen adsorption/absorption with palladium attachment, also plays a role in tuning the reaction kinetics and potentially the nanocluster morphology.

Conclusions

We studied the role of HCl in the structural evolution of palladium electrodeposits using liquid cell TEM and *post situ* SEM analyses. We found that aggregative electrochemical growth, based on self-limiting growth, surface diffusion, and recrystallization, explained the current time transients and the electron microscopy images obtained here. The addition of HCl in the electrodeposition bath transformed the morphology of palladium electrodeposits from non-porous and closed clusters with a circular projection to porous and open clusters with a non-spherical morphology. It is evident that HCl hinders the recrystallization of aggregated nanoclusters. We hypothesize this to be related to the adsorption of chloride ions and/or the competition between palladium adatom addition and hydrogen adsorption in the presence of HCl. Combining *in situ* and the *post situ* analyses provides valuable insight into the complex phenomena that occur during electrodeposition.

Experimental

Reagents

All chemicals were obtained in the highest available purity and used without further purification. Palladium (II) chloride powder ($\geq 99.9\%$) and hydrochloric acid (ACS reagent, 37%) were purchased from Sigma-Aldrich, Saint Louis, MO, USA. H_2PdCl_4 solutions were created by dissolving the palladium (II) chloride powder in HCl, and diluting the mixture in water followed by four hours of sonication. Electrolyte solutions were bubbled using nitrogen gas for 20 minutes to remove dissolved oxygen before *in situ* electrodeposition.

***In situ* liquid electrochemical TEM (LEC-TEM) system**

The *in situ* liquid electrochemical TEM system (Poseidon 500, Protochips Inc., Raleigh, NC, USA) used in this study was composed of a liquid cell at the tip of a TEM holder. The TEM holder included electrical and fluidic circuitry for interfacing the liquid cell with a potentiostat (Gamry Reference 600, Gamry Instruments Inc., Warminster, PA, USA) for electrochemical control and a syringe pump (Harvard 11 Elite standard infuse only syringe pump, Harvard Apparatus Inc., Holliston, MA, USA) for fluidic control. Two microfabricated chips with 50 nm silicon nitride membranes were sealed inside the liquid cell and *in situ* imaging was performed with electrons passing through the overlapped membranes. The commercially-available bottom chip (ECT24-CO, Protochips Inc., Raleigh, NC, USA) was used as a miniaturized electrochemical cell with carbon working electrode, Pt reference electrode, and Pt counter electrode and had 500 nm spacers. The top chip only contained SiN windows (EPB-52DF, Protochips Inc., Raleigh, NC, USA) with 150 nm spacers.

***In situ* electron microscopy and electrodeposition**

In situ chronoamperometry was performed in 5 mM H_2PdCl_4 with 0.015 M HCl and without HCl with solution flow rate of 5 $\mu\text{L}/\text{min}$. The current transients were obtained using the Gamry potentiostat. Real-time imaging was performed using a JEOL 2010F TEM operated at 200 kV. Bright-field scanning transmission electron microscope (BF-STEM) mode was performed under a beam dose of 21 electrons/frame. nm^2 . *In situ* images were acquired using a DigiScan II (Gatan, model 788) unit with a BF detector with time resolution of 0.555 s/frame. The *in situ* process was recorded as a video and *in situ* images were extracted from the videos. The experiments were performed using a flow rate of 5 $\mu\text{L}/\text{min}$. Assuming a constant cross sectional area for the fluid

having a width of 600 μm and a minimum thickness of 0.5 μm (imposed by the spacer dimension), we estimate the upper bound for the linear flow velocity to be 278 mm/s.

Simulation and particle analysis

Simulation of electric field distribution was conducted using COMSOL Multiphysics 4.3b (COMSOL Inc., Stockholm, Sweden) by applying Tertiary Current Distribution module, which considers mass transport through diffusion and migration through Nernst-Planck equation. Measurement of the diameter and size distribution of palladium particles was performed using ImageJ.

Post situ analysis

The *post situ* characterization of the structures grown on the carbon microelectrode was performed using the JEOL 7000 field emission SEM. The chips with the electrodeposited material were rinsed in DI water and air dried prior to analysis.

Supporting Information

- Figure S1 shows the *in situ* cyclic voltammogram of carbon electrode in solutions with and without HCl.
- Figure S2 shows simulation of the electric field distribution around the carbon working electrode used in liquid cell TEM experiments.
- Figure S3 shows the *in situ* chronoamperogram with electron beam on and off.
- Figure S4 shows the *in situ* chronoamperogram with the solution under static and flow conditions.
- Figure S5 shows the *in situ* chronoamperogram and *post situ* SEM images acquired in 5 mM H_2PdCl_4 solutions with 0.015 M HCl versus 0.5 M KCl.
- Figure S6 shows the size distribution of deposited palladium particles on carbon electrode used in liquid cell transmission electron microscopy in solutions with and without HCl.
- Figure S7 shows the integrated charge obtained from *in situ* chronoamperograms in 5 mM H_2PdCl_4 with and without HCl.
- Figure S8 shows the *in situ* chronomaperogram, *in situ* TEM images and *post situ* SEM images acquired in 5 mM H_2PdCl_4 solutions with 0.015 M HCl versus 0.015 M KCl.
- Supplementary Video 1 shows *in situ* electrodeposition in a solution of 5 mM H_2PdCl_4 .
- Supplementary Video 2 shows *in situ* electrodeposition in a solution of 5 mM H_2PdCl_4 with 0.015 M HCl.

Acknowledgement

We acknowledge financial support from Natural Sciences and Engineering Research Council (NSERC). L.S. is the Canada Research Chair in Miniaturized Biomedical Devices, and G.A.B. is the Canada Research Chair in Microscopy of Nanoscale Materials. Both Chairs are supported by the Canada Research Chairs Program. The microscopy work was carried out at the Canadian Centre for Electron Microscopy, a facility supported by the Canada Foundation for Innovation under the Major Science Initiative program, NSERC and McMaster University.

We also acknowledge Glynis de Silveira, Andreas Korinek, and Andy Duft for assistance with experimental establishment and discussions on image analysis.

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